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(71)Applicant : SUMITOMO CHEM CO LTD

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(72)Inventor : TAKEDA TAKASHI
ONO KEIJI
MIYAZAKI SUSUMU
TODA KENJI
SATO MINEO

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(54) FLUORESCENT SUBSTANCE FOR VACUUM ULTRAVIOLET-EXCITED LIGHT EMITTING DIODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a fluorescent substance for vacuum ultraviolet excited light emitting diodes having excellent emission brightness and little reduction in plasma exposure.

SOLUTION: This fluorescent substance comprises a compound expressed by general formula: $mM1O.nM2O.2M3O2$ (wherein M1 expresses ≥ 1 species selected from a group consisting of Ca, Sr and Ba; M2 expresses ≥ 1 species selected from a group consisting of Mg and Zn; M3 expresses ≥ 1 species selected from a group consisting of Si and Ge; $0.5 \leq m \leq 3.5$; $0.5 \leq n \leq 2.5$; when $m=n=1$, M1 expresses ≥ 2 species selected from a group consisting of Ca, Sr and Ba or Sr or Ba) containing ≥ 1 species selected from a group consisting of Eu and Mn as an activating agent. The a fluorescent substance has the same crystal structure as that of either one of diopside, akermanite or merwinite.

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(33) 優先権主張国 日本 (J P)

(71) 出願人 000002093

住友化学工業株式会社

大阪府大阪市中央区北浜 4 丁目 5 番33号

(72) 発明者 武田 隆史

茨城県つくば市北原 6 住友化学工業株式
会社内

(72) 発明者 大野 慶司

茨城県つくば市北原 6 住友化学工業株式
会社内

(74) 代理人 100093285

弁理士 久保山 隆 (外 2 名)

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(54) 【発明の名称】 真空紫外線励起発光素子用の蛍光体

(57) 【要約】

【課題】 発光輝度が高く、プラズマ暴露による輝度低下が少ない真空紫外線励起発光素子用の蛍光体を提供する。

【解決手段】 一般式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ (式中の M^1 は Ca、Sr および Ba からなる群より選ばれる 1 種以上、 M^2 は Mg および Zn からなる群より選ばれる 1 種以上、 M^3 は Si および Ge からなる群より選ばれる 1 種以上、 $0.5 \leq m \leq 3.5$ 、 $0.5 \leq n \leq 2.5$ 、ただし $m=n=1$ のときは M^1 は Ca、Sr および Ba からなる群より選ばれる 2 種以上または Sr または Ba である。) で表される化合物に付活剤として Eu および Mn からなる群より選ばれる 1 種以上が含有される真空紫外線励起発光素子用の蛍光体。ディオプサイド、オケルマナイト、メルウィナイトのいずれかと同じ結晶構造を有する上記記載の蛍光体。

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【特許請求の範囲】

【請求項1】一般式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、 M^3 はSiおよびGeからなる群より選ばれる1種以上、 $0.5 \leq m \leq 3.5$ 、 $0.5 \leq n \leq 2.5$ 、ただし $m=n=1$ のときは M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBaである。）で表される化合物に付活剤としてEu、Mnからなる群より選ばれる1種以上が含有されてなることを特徴とする真空紫外線励起発光素子用の蛍光体。

【請求項2】請求項1記載の真空紫外線励起発光素子用の蛍光体であって、ディオプサイド（Diopside、透輝石）と同じ結晶構造を有する蛍光体。

【請求項3】一般式 $(M^4)_{1-a}Eu_a)(M^5)_{1-b}Mn_b)M^{62}O_6$ （式中の M^4 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBa、 M^5 はMgおよびZnからなる群より選ばれる1種以上、 M^6 はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq a \leq 0.5$ 、 $0 \leq b \leq 0.5$ 、 $0 < a+b$ 。）で表される組成を有する請求項2記載の蛍光体。

【請求項4】一般式 $Ca_{1-c-d}Sr_cEu_dMgSi_2O_6$ （ $0 < c \leq 0.1$ 、 $0 < d \leq 0.1$ 。）で表される組成を有する請求項2記載の蛍光体。

【請求項5】請求項1記載の真空紫外線励起発光素子用の蛍光体であって、オケルマナイト（Akermanite、オケルマン石）と同じ結晶構造を有する蛍光体。

【請求項6】一般式 $(M^7)_{1-e}Eu_e)_2(M^8)_{1-f}Mn_f)M^{92}O_7$ （式中の M^7 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^8 はMgおよびZnからなる群より選ばれる1種以上、 M^9 はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq e \leq 0.5$ 、 $0 \leq f \leq 0.5$ 、 $0 < e+f$ 。）で表される組成を有する請求項5記載の蛍光体。

【請求項7】一般式 $(M^{10})_{1-g}Eu_g)_2M^{11}Si_2O_7$ （式中の M^{10} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{11} はMgおよびZnからなる群から選ばれる1種以上、 $0.001 \leq g \leq 0.1$ 。）で表される組成を有する請求項5記載の蛍光体。

【請求項8】一般式 $(M^{12})_{1-h}Eu_h)(M^{13})_{1-i}Mn_i)2M^{14}O_7$ （式中の M^{12} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{13} はMgおよびZnからなる群より選ばれる1種以上、 M^{14} はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq h \leq 0.5$ 、 $0 \leq i \leq 0.5$ 、 $0 < h+i$ 。）で表される組成を有する請求項5記載の蛍光体。

【請求項9】請求項1記載の真空紫外線励起発光素子用の蛍光体であって、メルウィナイト（Merwinite）と同じ結晶構造を有する蛍光体。

【請求項10】一般式 $(M^{15})_{1-j}Eu_j)_3(M^{16})_{1-k}Mn$

$k)M^{17}O_8$ （式中の M^{15} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{16} はMgおよびZnからなる群より選ばれる1種以上、 M^{17} はSiおよびGeからなる群より選ばれた1種以上、 $0 \leq j \leq 0.5$ 、 $0 \leq k \leq 0.5$ 、 $0 < j+k$ 。）で表される組成を有する請求項9記載の蛍光体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、プラズマディスプレイパネル（以下「PDP」という。）および希ガスランプなどの真空紫外線励起発光素子に好適な蛍光体に關するものである。

【0002】

【従来の技術】真空紫外線等によって励起して発光させる蛍光体はすでに知られている。例えば、Ba、Mg、Al、Oと付活剤（Eu）とからなるBaMgAl₁₀O₁₇:Euが真空紫外線励起発光素子用の青色蛍光体として、また例えば、Zn、Si、Oと付活剤（Mn）とからなるZn₂SiO₄:Mnが緑色蛍光体として、また例えば、Y、Gd、B、Oと付活剤（Eu）とからなる（Y、Gd）BO₃:Eu赤色蛍光体として実用化されており、PDPや希ガスランプ等の真空紫外線励起発光素子用に用いられている。

【0003】

しかしながら、これら真空紫外線励起発光素子用の蛍光体にはさらなる輝度の向上が望まれていた。また、PDPおよび希ガスランプ等の真空紫外線励起発光素子においては、希ガス中で放電を行いプラズマを生成させることにより真空紫外線を発生しているが、プラズマに暴露されることにより蛍光体の輝度が低下する問題があり、プラズマ暴露による輝度低下の少ない真空紫外線励起発光素子用の蛍光体が求められており、上記したようなアルミン酸塩、ケイ酸塩、ホウ酸塩からなる蛍光体が検討されている。ケイ酸塩からなる蛍光体としては、例えば、Extended abstracts of the sixth international conference on the science and technology of display phosphors, 21-24には真空紫外線励起発光素子用の蛍光体としてCaMgSi₂O₆:Euが開示されているが、輝度が十分ではなかった。なお、米国特許第5839718号明細書にはSr_{1.995}MgSi₂O₇:Eu_{0.005}, Dy_{0.025}, Cl_{0.025}およびSr_{0.445}Ba_{1.55}MgSi₂O₇:Eu_{0.005}, Dy_{0.025}, Cl_{0.025}が開示されているが、暗所の表示用等に用いられる蓄光体用の蛍光体であり、真空紫外線励起については記載されていなかった。

【0004】

【発明が解決しようとする課題】本発明の目的は、輝度が高く、プラズマ暴露による輝度低下が少ない真空紫外線励起発光素子用の蛍光体を提供することにある。

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【0005】

【課題を解決するための手段】本発明者らは、かかる状況下、上記の課題を解決すべく鋭意研究を重ねた結果、真空紫外線励起発光素子用には、ケイ酸塩またはゲルマン酸塩蛍光体の中でも、一般式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、 M^3 はSiおよびGeからなる群より選ばれる1種以上、 $0.5 \leq m \leq 3.5$ 、 $0.5 \leq n \leq 2.5$ 、ただし $m=n=1$ のとき、 M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBaである。）で表される化合物に付活剤としてEuおよびMnからなる群より選ばれる1種以上が含有されてなる特定組成のケイ酸塩またはゲルマン酸塩蛍光体は輝度が高くかつプラズマ暴露による輝度低下が少ないことを見出し、本発明を完成するに至った。

【0006】すなわち本発明は、以下の(1)～(10)に関するものである。

(1) 一般式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、 M^3 はSiおよびGeからなる群より選ばれる1種以上、 $0.5 \leq m \leq 3.5$ 、 $0.5 \leq n \leq 2.5$ 、ただし $m=n=1$ のときは M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBaである。）で表される化合物に付活剤としてEuおよびMnからなる群より選ばれる1種以上が含有された真空紫外線励起発光素子用の蛍光体。

(2) ディオプサイド(Diopside、透輝石)と同じ結晶構造を有する上記(1)記載の蛍光体。

(3) 一般式 $(M^4)_a(M^5)_b(M^6)_cO_6$ （式中の M^4 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBa、 M^5 はMgおよびZnからなる群より選ばれる1種以上、 M^6 はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq a \leq 0.5$ 、 $0 \leq b \leq 0.5$ 、 $0 < a+b$ 。）により表される組成を有する上記(2)記載の蛍光体。

(4) 一般式 $Ca_{1-c-d}Sr_cEu_dMgSi_2O_6$ （ $0 < c \leq 0.1$ 、 $0 < d \leq 0.1$ 。）で表される上記(2)記載の蛍光体。

(5) 上記(1)記載の真空紫外線励起発光素子用の蛍光体であって、オケルマナイト(Akermanite、オケルマン石)と同じ結晶構造を有する蛍光体。

(6) 一般式 $(M^7)_e(M^8)_f(M^9)_gO_7$ （式中の M^7 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^8 はMgおよびZnからなる群より選ばれる1種以上、 M^9 はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq e \leq 0.5$ 、 $0 \leq f \leq 0.5$ 、 $0 < e+f$ 。）で表される組成を有する上記(5)記載の蛍光体。

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(7) 一般式 $(M^{10})_l(M^{11})_i(M^{12})_j(M^{13})_k(M^{14})_mO_7$ （式中の M^{10} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{11} はMgおよびZnからなる群より選ばれる1種以上、 $0.001 \leq g \leq 0.1$ ）で表される組成を有する上記(5)記載の蛍光体。

(8) 一般式 $(M^{12})_h(M^{13})_i(M^{14})_j(M^{15})_k(M^{16})_lO_7$ （式中の M^{12} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{13} はMgおよびZnからなる群より選ばれる1種以上、 M^{14} はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq h \leq 0.5$ 、 $0 \leq i \leq 0.5$ 、 $0 < h+i$ 。）で表される組成を有する上記(5)記載の蛍光体。

(9) 上記(1)記載の真空紫外線励起発光素子用の蛍光体であって、メルウィナイト(Merwinite)と同じ結晶構造を有する蛍光体。

(10) 一般式 $(M^{15})_j(M^{16})_k(M^{17})_l(M^{18})_m(M^{19})_nO_8$ （式中の M^{15} はCa、SrおよびBaからなる群より選ばれる1種以上、 M^{16} はMgおよびZnからなる群より選ばれる1種以上、 M^{17} はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq j \leq 0.5$ 、 $0 \leq k \leq 0.5$ 、 $0 < j+k$ 。）で表される組成を有する上記(9)記載の蛍光体。

【0007】

【発明の実施の形態】以下に本発明について詳しく説明する。本発明の真空紫外線励起発光素子用の蛍光体は、一般式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる1種以上、 M^2 はMgおよびZnからなる群より選ばれる1種以上、 M^3 はSiおよびGeからなる群より選ばれる1種以上、 $0.5 \leq m \leq 3.5$ 、 $0.5 \leq n \leq 2.5$ 、ただし $m=n=1$ のとき、 M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBaである。）を母結晶とし、付活剤としてEuおよびMnからなる群より選ばれる1種以上が含有されてなることを特徴とし、ディオプサイド、オケルマナイト、メルウィナイトと同じ結晶構造をもつものが好ましい。

【0008】ディオプサイド(Diopside、透輝石)と同型の結晶構造を有する場合の中でも、上記

(1)の一般式において $m=1$ および $n=1$ の場合の一つである一般式 $(M^4)_a(M^5)_b(M^6)_cO_6$ （式中の M^4 はCa、SrおよびBaからなる群より選ばれる2種以上またはSrまたはBa、 M^5 はMgおよびZnからなる群より選ばれる1種以上、 M^6 はSiおよびGeからなる群より選ばれる1種以上、 $0 \leq a \leq 0.5$ 、 $0 \leq b \leq 0.5$ 、 $0 < a+b$ 。）で表される組成を有する蛍光体が真空紫外線励起発光素子用として好ましい。さらに、ディオプサイド(Diopside、透輝石)と同型の結晶構造を有する場合の中でも、上記(1)の一般式において $m=1$ および $n=1$ の場合の一つでありCaとSrを含む一般式 $Ca_{1-c-d}Sr_cEu_d$

(4)

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$MgSi_2O_6$ ($0 < c \leq 0.1$, $0 < d \leq 0.1$.) で表される組成を有する蛍光体がさらに好ましい。

【0009】オケルマナイト (Akermanite、オケルマン石) と同じ結晶構造を有する場合の中でも、上記(1)の一般式において $m=2$ および $n=1$ の場合の一つである一般式 $(M^{7l}-eEu_e)_2(M^{8l}-fMn_f)M^{9l}O_7$ (式中の M^7 は Ca、Sr および Ba からなる群より選ばれる1種以上、 M^8 は Mg および Zn からなる群より選ばれる1種以上、 M^9 は Si および Ge からなる群より選ばれる1種以上、 $0 \leq e \leq 0.5$ 、 $0 \leq f \leq 0.5$ 、 $0 < e + f$.) で表される組成を有する蛍光体が真空紫外線励起発光素子用として好ましい。さらに、前記一般式において $f=0$ で M^9 が Si の場合の一般式 $(M^{10l}-gEu_g)_2M^{11l}Si_2O_7$ (式中の M^{10} は Ca、Sr および Ba からなる群より選ばれる1種以上、 M^{11} は Mg および Zn からなる群から選ばれる1種以上、 $0.001 \leq g \leq 0.1$) で表される組成を有する蛍光体がさらに好ましい。

【0010】また、オケルマナイトと同じ結晶構造を有する場合の中でも、上記(1)の一般式において $m=1$ および $n=2$ の場合の一つである一般式一般式 $(M^{12l}-hEu_h)(M^{13l}-iMn_i)_2M^{14l}O_7$ (式中の M^{12} は Ca、Sr および Ba からなる群より選ばれる1種以上、 M^{13} は Mg および Zn からなる群より選ばれる1種以上、 M^{14} は Si および Ge からなる群より選ばれる1種以上、 $0 \leq h \leq 0.5$ 、 $0 \leq i \leq 0.5$ 、 $0 < h + i$.) で表される組成を有する蛍光体も真空紫外線励起発光素子用として好ましい。

【0011】メルウィナイト (Merwinite) と同型の結晶構造を有する場合の中でも、上記(1)の一般式において $m=3$ および $n=1$ の場合の一つである、一般式 $(M^{15l}-jEu_j)_3(M^{16l}-kMn_k)M^{17l}O_8$ (式中の M^{15} は Ca、Sr および Ba からなる群より選ばれる1種以上、 M^{16} は Mg および Zn からなる群より選ばれる1種以上、 M^{17} は Si および Ge からなる群より選ばれた1種以上、 $0 \leq j \leq 0.5$ 、 $0 \leq k \leq 0.5$ 、 $0 < j + k$.) で表される組成を有する蛍光体が真空紫外線励起発光素子用として好ましい。上記ディオプサイド、オケルマナイト、メルウィナイトと同じ結晶構造を持つ蛍光体のなかでも、ディオプサイド、メルウィナイトと同じ結晶構造を持つ蛍光体が好ましく、ディオプサイドと同じ結晶構造を持つ蛍光体がさらに好ましい。

【0012】次に本発明の蛍光体の製造方法について説明する。本発明の蛍光体を製造するための原料となるカルシウム源、ストロンチウム源、バリウム源としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99.9%以上)の酸化物が使用できる。マグネシウム源、亜鉛源となる原料として

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は、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。ケイ素源、ゲルマニウム源となる原料としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。

【0013】付活剤となるユーロピウム、マンガンを含む原料としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。

【0014】本発明の蛍光体の製造方法は特に限定されるものではなく、例えば、上記それぞれの原料を混合し焼成することにより製造することができる。好ましい組成の一つである一般式 $(M^{4l}-aEu_a)(M^{5l}-bMn_b)M^{6l}O_6$ (式中の M^4 は Ca、Sr および Ba からなる群より選ばれる2種以上または Sr または Ba、 M^5 は Mg および Zn からなる群より選ばれる1種以上、 M^6 は Si および Ge からなる群より選ばれる1種以上、 $0 \leq a \leq 0.5$ 、 $0 \leq b \leq 0.5$ 、 $0 < a + b$.) で表される組成を有する蛍光体は、上記原料を所定の組成となるように秤量し配合し、混合して焼成することにより製造することができる。これらの原料の混合には通常工業的に用いられているボールミル、V型混合機、または攪拌装置等を用いることができる。

【0015】混合した後、例えば1000℃から1500℃の温度範囲にて1~100時間焼成することにより本発明の蛍光体が得られる。原料に水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものが使用した場合、本焼成の前に、例えば600℃から900℃の温度範囲にて仮焼することも可能である。焼成雰囲気としては、特に限定されるものではないが、例えば水素を0.1~10体積%含む窒素やアルゴン等の還元性雰囲気中で焼成することが好ましい。また仮焼の雰囲気は大気雰囲気、還元性雰囲気のいずれでもよい。また、反応を促進するために、適量のフラックスを添加してもよい。

【0016】さらに、上記方法にて得られる蛍光体を、例えばボールミル、ジェットミル等を用いて粉碎することができる。また、洗浄、分級することができる。得られる蛍光体の結晶性を高めるために、再焼成を行うこともできる。

【0017】以上のようにして得られる本発明の蛍光体は真空紫外線励起によって高い輝度が得られ、プラズマ暴露による輝度低下が少ない。さらに、PDPおよび希ガスランプの製造においては、蛍光体にバインダーを加えて溶媒に分散させ、発光部に塗布して500℃程度で熱処理してバインダーを除去することにより蛍光体を設

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置する工程が一般的であるが、本発明の蛍光体は、この熱処理工程における輝度低下も少ない。従って、本発明の蛍光体をPDPおよび希ガスランプなどの真空紫外線励起発光素子用に用いた場合、高輝度で寿命の長いPDPおよび希ガスランプが実現できるので、真空紫外線励起発光素子用として好適である。

【0018】本発明の蛍光体は真空紫外域以外の紫外線、X線および電子線などによっても励起可能であり、真空紫外域以外の紫外線、X線および電子線を励起源とした素子にも用いることができる。

【0019】

【実施例】次に、本発明を実施例によりさらに詳しく説明するが、本発明はこれらの実施例に限定されるものではない。

【0020】実施例1

炭酸カルシウム（和光純薬工業（株）製） CaCO_3 、炭酸ストロンチウム（和光純薬工業（株）製） SrCO_3 、酸化ユーロピウム（信越化学工業（株）製） Eu_2O_3 、塩基性炭酸マグネシウム（和光純薬工業（株）製） $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ 、酸化珪素（和光純薬工業（株）製） SiO_2 各原料を $\text{CaCO}_3 : \text{SrCO}_3 : \text{Eu}_2\text{O}_3 : (\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} : \text{SiO}_2$ のモル比が0.9215 : 0.0485 : 0.015 : 0.2 : 2になるように配合し混合した後、2体積% H_2 含有Ar雰囲気中で1200℃の温度で2時間焼成、解砕後、再度2体積% H_2 含有Ar雰囲気中で1200℃の温度で2時間焼成した。このようにして、組成式が $\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6$ で表される蛍光体を得た。この蛍光体に、6.7 Pa (5×10^{-2} Torr) 以下の真空槽内で、得られた蛍光体にエキシマ146 nmランプ（ウシオ電機社製、H0012型）を用いて紫外線を照射したところ、青色の発光を示し、輝度は24 cd/m²を示した。

【0021】得られた蛍光体を、空気中で500℃、30分間熱処理を行った。蛍光体を取り出して輝度を測定した結果、熱処理前に比較して輝度は全く低下しなかった。

【0022】得られた熱処理前の蛍光体を、圧力が13.2 Paで5体積%Xe-95体積%Neの組成の雰囲気中に設置し、10 Wのプラズマに30分間、ついで50 Wのプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、プラズマ曝露前に比較して輝度は全く低下しなかった。

【0023】得られた熱処理、プラズマ曝露前の蛍光体を、空気中で500℃、30分間熱処理を行った。次いで、圧力が13.2 Paで5体積%Xe-95体積%Neの組成の雰囲気中に設置し、10 Wのプラズマに30分間、ついで50 Wのプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、熱処理、プラズマ曝露前に比較して輝度の低下は4%であった。

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【0024】実施例2

炭酸ストロンチウム（和光純薬工業（株）製） SrCO_3 、炭酸バリウム（和光純薬工業（株）製） BaCO_3 、酸化ユーロピウム（信越化学工業（株）製） Eu_2O_3 、塩基性炭酸マグネシウム（和光純薬工業（株）製） $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ 、酸化珪素（和光純薬工業（株）製） SiO_2 各原料を $\text{SrCO}_3 : \text{BaCO}_3 : \text{Eu}_2\text{O}_3 : (\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} : \text{SiO}_2$ のモル比が2.28 : 0.57 : 0.075 : 0.2 : 2になるように配合、混合した後、2体積% H_2 含有Ar雰囲気中で1200℃の温度で2時間焼成した。このようにして、組成式が $\text{Sr}_{2.28}\text{Ba}_{0.57}\text{Eu}_{0.15}\text{MgSi}_2\text{O}_8$ で表される蛍光体を得た。この蛍光体に、6.7 Pa (5×10^{-2} Torr) 以下の真空槽内で、得られた蛍光体にエキシマ146 nmランプ（ウシオ電機社製、H0012型）を用いて紫外線を照射したところ、青色の発光を示し、輝度は30 cd/m²を示した。

【0025】実施例3

炭酸バリウム（関東化学（株）製） BaCO_3 、酸化ユーロピウム（信越化学工業（株）製） Eu_2O_3 、酸化マグネシウム（関東化学（株）製） MgO 、酸化珪素（（株）高純度化学研究所製） SiO_2 各原料を $\text{BaCO}_3 : \text{Eu}_2\text{O}_3 : \text{MgO} : \text{SiO}_2$ のモル比が1.98 : 0.01 : 1 : 2になるように配合し、また、生成物1モルに対して B_2O_3 をフラックスとして0.1モル添加し、アセトン中、乳鉢で十分湿式混合し、乾燥した。得られた混合原料をステンレス製の金型に入れ、40 MPaの圧力で加圧して直径15 mm×厚さ3 mmの円形ペレットに成形した。得られたペレットをアルミナ坩堝に入れ、5体積% H_2 -95体積%Ar雰囲気中で1200℃で3時間焼成した。このようにして、組成式が $\text{Ba}_{1.98}\text{Eu}_{0.02}\text{MgSi}_2\text{O}_7$ で表される蛍光体を得た。この蛍光体に、6.7 Pa (5×10^{-2} Torr) 以下の真空槽内で、得られた蛍光体にエキシマ146 nmランプ（ウシオ電機社製、H0012型）を用いて紫外線を照射したところ、緑色の発光を示し、輝度は95 cd/m²を示した。

【0026】実施例4

($\text{Sr}_{0.99}\text{Eu}_{0.01}$) $_2\text{MgSi}_2\text{O}_7$ を製造するにあたり、出発原料として、炭酸ストロンチウム（関東化学（株）製） SrCO_3 、酸化ユーロピウム（信越化学工業（株）製） Eu_2O_3 、酸化マグネシウム（関東化学（株）製） MgO 、酸化珪素（（株）高純度化学研究所製） SiO_2 を用いた。これら原料を $\text{SrCO}_3 : \text{Eu}_2\text{O}_3 : \text{MgO} : \text{SiO}_2$ のモル比が1.98 : 0.01 : 1 : 2になるように配合し、また、生成物($\text{Sr}_{0.99}\text{Eu}_{0.01}$) $_2\text{MgSi}_2\text{O}_7$ 1モルに対して B_2O_3 をフラックスとして0.1モル添加し、アセトン中、乳鉢で十分湿式混合し、乾燥した。得られた混合原料をステンレス

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製の金型に入れ、40MPaの圧力で加圧して直径15mm×厚さ3mmの円形ペレットに成形した。得られたペレットをアルミナ坩堝に入れ、5% H_2 -95%Ar雰囲気中で1200℃で3時間焼成した。焼成後得られた試料に、波長254nmまたは365nmの紫外線を照射すると、いずれの場合も高輝度の水色発光を示した。6.7Pa(5×10^{-2} Torr)以下の真空槽内でエキシマ146nmランプ(ウシオ電機社製)を用いて真空紫外線を照射したところ、水色の発光を示し、輝度は25cd/cm²を示した。

【0027】実施例5

(Sr_{0.99}Eu_{0.01})₂ZnSi₂O₇を製造するにあたり、出発原料として、炭酸ストロンチウムSrCO₃、酸化ユーロピウムEu₂O₃、酸化亜鉛ZnO、酸化珪素SiO₂を用いた。これら原料をSrCO₃:Eu₂O₃:ZnO:SiO₂のモル比が1.98:0.01:1:2になるように配合し、フラックスとして生成物(Sr_{0.99}Eu_{0.01})₂ZnSi₂O₇1モルに対してB₂O₃を0.1モル添加し、アセトン中で乳鉢で十分湿式混合し、乾燥した。得られた混合原料をステンレス製の金型に入れ、40MPaの圧力で加圧して直径15mm×厚さ3mmの円形ペレットに成形した。得られたペレットをアルミナ坩堝に入れ、5% H_2 -95%Ar雰囲気中で1200℃で3時間焼成した。焼成後得られた試料につき、254nmもしくは365nmの紫外線にて励起するといずれも高輝度の青緑色発光を示した。6.7Pa(5×10^{-2} Torr)以下の真空槽内で得られた蛍光体にエキシマ146nmランプ(ウシオ電機社製)を用いて真空紫外線を照射したところ、青緑色の発光を示した。

【0028】比較例1

炭酸カルシウム(和光純薬工業(株)製)CaCO₃、酸化ユーロピウム(信越化学工業(株)製)Eu₂O₃、塩基性炭酸マグネシウム(和光純薬工業(株)製)(MgCO₃)₄Mg(OH)₂·5H₂O、酸化珪素(和光

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純薬工業(株)製)SiO₂各原料をCaCO₃:Eu₂O₃:(MgCO₃)₄Mg(OH)₂·5H₂O:SiO₂のモル比が0.95:0.025:0.2:2になるように配合、混合した後、2体積% H_2 含有Ar雰囲気中で1200℃の温度で2時間焼成した。このようにして、組成式がCa_{0.95}Eu_{0.05}MgSi₂O₆で表される蛍光体を得た。この蛍光体に、6.7Pa(5×10^{-2} Torr)以下の真空槽内で、得られた蛍光体にエキシマ146nmランプ(ウシオ電機社製、H0012型)を用いて紫外線を照射したところ、青色の発光を示し、輝度は12cd/m²を示した。

【0029】比較例2

市販の青色発光蛍光体BaMgAl₁₀O₁₇:Euを、空气中で500℃、30分間熱処理を行った。蛍光体を取り出して輝度を測定した結果、熱処理前に比較して輝度が1%低下した。

【0030】上記市販の青色発光蛍光体を、圧力が13.2Paで5体積%Xe-95体積%Neの組成の雰囲気中に設置し、10Wのプラズマに30分間、ついで50Wのプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、プラズマ曝露前に比較して輝度が25%低下した。

【0031】上記市販の青色発光蛍光体を、空气中で500℃、30分間熱処理を行った。次いで、圧力が13.2Paで5体積%Xe-95体積%Neの組成の雰囲気中に設置し、10Wのプラズマに30分間、ついで50Wのプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、熱処理、プラズマ曝露前に比較して輝度が28%低下した。

【0032】

【発明の効果】本発明の蛍光体は輝度が高く、プラズマ暴露による輝度低下が少なく、特にPDPや希ガスランプなどの真空紫外線励起発光素子用に好適であり、高輝度の真空紫外線励起発光素子を実現できるので、工業的に極めて有用である。

フロントページの続き

(72)発明者 宮崎 進
茨城県つくば市北原6 住友化学工業株式会社内
(72)発明者 戸田 健司
新潟県新潟市五十嵐中島二丁目12番5号
(72)発明者 佐藤 峰夫
新潟県新潟市五十嵐一の町7793番地12

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CLAIMS

[Claim(s)]

[Claim 1] general formula $mM1O \cdot nM2O \cdot 2M3O2$ (M1 in a formula is chosen from the group which consists of calcium, Sr, and Ba — one or more sorts) One or more sorts chosen from the group which M2 becomes from Mg and Zn, one or more sorts chosen from the group which M3 becomes from Si and germanium, M1 is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba at the time of $0.5 \leq m \leq 3.5$, $0.5 \leq n \leq 2.5$, however $m=n=1$. The fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices characterized by one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator coming to contain.

[Claim 2] The fluorescent substance which is a fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices according to claim 1, and has the same crystal structure as a DIOPU side (Diopside, diopside).

[Claim 3] general formula $(M4)_{1-a}Eua(M5)_{1-b}MnbM6_2O_6$ (M4 in a formula — calcium —) one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, and $0 \leq a+b$. The fluorescent substance according to claim 2 which has the presentation expressed.

[Claim 4] The fluorescent substance according to claim 2 which has the presentation expressed with general formula $Ca_{1-c}Sr_cEu_dMgSi_2O_6$ ($0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$).

[Claim 5] The fluorescent substance which is a fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices according to claim 1, and has the same crystal structure as akermanite (Akermanite, OKERUMAN stone).

[Claim 6] general formula $(M7)_{1-e}Eue2(M8)_{1-f}MnfM9_2O_7$ (M7 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M8 becomes from Mg and Zn, one or more sorts chosen from the group which M9 becomes from Si and germanium, $0 \leq e \leq 0.5$, $0 \leq f \leq 0.5$, and $0 \leq e+f$. The fluorescent substance according to claim 5 which has the presentation expressed.

[Claim 7] The fluorescent substance according to claim 5 which has the presentation expressed with general formula $(M10)_{1-g}Eug2M11Si_2O_7$ (one or more sorts chosen from the group which M10 in a formula becomes from calcium, Sr, and Ba, one or more sorts chosen from the group which M11 becomes from Mg and Zn, $0.001 \leq g \leq 0.1$).

[Claim 8] general formula $(M12)_{1-h}Euh(M13)_{1-i}Mni2M14_2O_7$ (M12 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M13 becomes from Mg and Zn, one or more sorts chosen from the group which M14 becomes from Si and germanium, $0 \leq h \leq 0.5$, $0 \leq i \leq 0.5$, and $0 \leq h+i$. The fluorescent substance according to claim 5 which has the presentation expressed.

[Claim 9] The fluorescent substance which is a fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices according to claim 1, and has the same crystal structure as a merwinite (Merwinite).

[Claim 10] general formula $(M15)_{1-j}Euj3(M16)_{1-k}MnkM17_2O_8$ (M15 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M16 becomes from Mg and Zn, one or more sorts chosen from the group which M17 becomes from Si and germanium, $0 \leq j \leq 0.5$, $0 \leq k \leq 0.5$, and $0 \leq j+k$. The fluorescent substance according to claim 9 which has the presentation expressed.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the suitable fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (henceforth "PDP"), and a rare-gas lamp.

[0002]

[Description of the Prior Art] The fluorescent substance made to excite and emit light with vacuum ultraviolet radiation etc. is already known. BaMgAl₁₀O₁₇:Eu which consists of Ba, Mg, aluminum, O, and an activator (Eu) as a blue fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices for example, for example Zn₂SiO₄:Mn which consists of Zn, Si, O, and an activator (Mn) as a green fluorescent substance for example It is put in practical use as a BO₃:Eu red fluorescent substance which consists of Y, Gd, B, O, and an activator (Eu) (Y, Gd), and is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp.

[0003] However, the fluorescent substance for these vacuum-ultraviolet-radiation excitation light emitting devices was expected improvement in the further brightness. Moreover, although vacuum ultraviolet radiation is generated by discharging in rare gas and making the plasma generate in vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, by being exposed to the plasma, there is a problem to which the brightness of a fluorescent substance falls, the fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices with little brightness lowering by plasma exposure is called for, and the fluorescent substance which consists of an aluminate which was described above, a silicate, and a borate is examined. As a fluorescent substance which consists of a silicate, it is Extended, for example. abstracts of the sixth international conference on the science and technology of display Brightness was not enough although CaMgSi₂O₆:Eu was indicated by phosphors and 21-24 as a fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices. In addition, although Sr_{1.995}MgSi₂O₇:Eu_{0.005}, Dy_{0.025} and Cl_{0.025} and Sr_{0.445}Ba_{1.55}MgSi₂O₇:Eu_{0.005}, and Dy_{0.025} and Cl_{0.025} were indicated by the U.S. Pat. No. 5839718 description, it is the fluorescent substance for luminous objects used for the display of a dark place, and vacuum-ultraviolet-radiation excitation was not indicated.

[0004]

[Problem(s) to be Solved by the Invention] The object of this invention has high brightness and offering few fluorescent substances for vacuum-ultraviolet-radiation excitation light emitting devices has the brightness lowering by plasma exposure.

[0005]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved under this situation, this invention persons to vacuum-ultraviolet-radiation excitation light emitting devices the inside of a silicate or a germane acid chloride fluorescent substance — general formula mM₁O-nM₂O.2M₃O₂ (M₁ in a formula — calcium —) One or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M₂ becomes from Mg and Zn, M₁ is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba at the time of one or more sorts chosen from the group which M₃ becomes from Si and germanium, 0.5<=m<=3.5, 0.5<=n<=2.5, however m=n=1. Brightness is high and the silicate or germane acid chloride fluorescent substance of a specific presentation which one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator come to contain came to complete a header and this invention for there being little brightness lowering by plasma exposure.

[0006] That is, this invention relates to the following (1) - (10).

(1) general formula mM₁O-nM₂O.2M₃O₂ (M₁ in a formula — calcium —) One or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M₂ becomes from Mg and Zn, M₁ is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba at the time of one or more sorts chosen from the group which M₃ becomes from Si and germanium, 0.5<=m<=3.5, 0.5<=n<=2.5, however m=n=1. The fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices which one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator contained.

(2) The fluorescent substance of the above-mentioned (1) publication which has the same crystal structure as a DIOPU side (Diopside, diopside).

(3) general formula (M₄₁-aEua) (M₅₁-bMnb) M₆2O₆ (M₄ in a formula — calcium —) one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M₅ become from Mg and Zn, one or more sorts chosen from the group which M₆ becomes from Si and germanium, 0<=a<=0.5, 0<=b<=0.5, and 0<a+b. The fluorescent substance of the above-mentioned (2) publication which has the presentation expressed.

(4) The fluorescent substance of the above-mentioned (2) publication expressed with general formula calcium_{1-c}dSrcEudMgSi₂O₆ (0< c<=0.1, 0< d<=0.1.).

(5) The fluorescent substance which is a fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of the above-mentioned (1) publication, and has the same crystal structure as akermanite (Akermanite, OKERUMAN stone).

(6) general formula (M₇₁-eEue) 2(M₈₁-fMnf) M₉2O₇ (M₇ in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M₈ becomes from Mg and Zn, one or more sorts chosen from the group which M₉ becomes from Si and germanium, 0<=e<=0.5, 0<=f<=0.5, and 0<e+f. The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed.

(7) The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed with

general formula (M101-gEug) 2M11Si 2O7 (one or more sorts chosen from the group which M10 in a formula becomes from calcium, Sr, and Ba, one or more sorts chosen from the group which M11 becomes from Mg and Zn, $0.001 \leq g \leq 0.1$).

(8) general formula (M121-hEuh) (M131-iMni) 2M142O7 (M12 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M13 becomes from Mg and Zn, one or more sorts chosen from the group which M14 becomes from Si and germanium, $0 \leq h \leq 0.5$, $0 \leq i \leq 0.5$, and $0 < h+i$. The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed.

(9) The fluorescent substance which is a fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of the above-mentioned (1) publication, and has the same crystal structure as a merwinite (Merwinite).

(10) general formula (M151-jEuj) 3(M161-kMnk) M172O8 (M15 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M16 becomes from Mg and Zn, one or more sorts chosen from the group which M17 becomes from Si and germanium, $0 \leq j \leq 0.5$, $0 \leq k \leq 0.5$, and $0 < j+k$. The fluorescent substance of the above-mentioned (9) publication which has the presentation expressed.

[0007]

[Embodiment of the Invention] This invention is explained in detail below. The fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of this invention general formula $mM1 \ O-nM2O.2M3O2$ (M1 in a formula is chosen from the group which consists of calcium, Sr, and Ba — one or more sorts) At the time of one or more sorts chosen from the group which M2 becomes from Mg and Zn, one or more sorts chosen from the group which M3 becomes from Si and germanium, $0.5 \leq m \leq 3.5$, $0.5 \leq n \leq 2.5$, however $m=n=1$ M1 is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba. What considers as a mother crystal, is characterized by one or more sorts chosen from the group which consists of Eu and Mn as an activator coming to contain, and has the same crystal structure as a DIOPU side, akermanite, and a merwinite is desirable.

[0008] Even in the inside in the case of having the crystal structure of a DIOPU side (Diopside, diopside) and isomorphism general formula (M41-aEua) (M51-bMnb) M62O6 (M4 in a formula — calcium —) which is one in $m=1$ and $n=1$ in the general formula of the above (1) one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, and $0 < a+b$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices. Furthermore, the fluorescent substance which has the presentation expressed with general formula calcium1-c-dSrcEudMgSi 2O6 ($0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$) which is one in $m=1$ and $n=1$ in the general formula of the above (1), and contains calcium and Sr even in the inside in the case of having the crystal structure of a DIOPU side (Diopside, diopside) and isomorphism is still more desirable.

[0009] Even in the inside in the case of having the same crystal structure as akermanite (Akermanite, OKERUMAN stone) general formula (M71-eEue) 2(M81-fMnf) M92O7 (M7 in a formula — calcium —) which is one in $m=2$ and $n=1$ in the general formula of the above (1) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M8 becomes from Mg and Zn, one or more sorts chosen from the group which M9 becomes from Si and germanium, $0 \leq e \leq 0.5$, $0 \leq f \leq 0.5$, and $0 < e+f$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices. furthermore, the fluorescent substance which has the presentation expressed with general formula (M101-gEug) 2M11Si 2O7 (one or more sorts chosen from the group which M10 in a formula becomes from calcium, Sr, and Ba, one or more sorts chosen from the group which M11 becomes from Mg and Zn, $0.001 \leq g \leq 0.1$) in case M9 are Si in $f=0$ in said general formula is still more desirable.

[0010] general formula general formula (M121-hEuh) (M131-iMni) 2M142O7 [moreover,] (M12 in a formula — calcium —) which is one in $m=1$ and $n=2$ in the general formula of the above (1) also in the inside in the case of having the same crystal structure as akermanite one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M13 becomes from Mg and Zn, one or more sorts chosen from the group which M14 becomes from Si and germanium, $0 \leq h \leq 0.5$, $0 \leq i \leq 0.5$, and $0 < h+i$. The fluorescent substance which has the presentation expressed is also desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0011] Even in the inside in the case of having the crystal structure of a merwinite (Merwinite) and isomorphism In the general formula of the above (1), it is one in $m=3$ and $n=1$. general formula (M151-jEuj) 3(M161-kMnk) M172O8 (M15 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M16 becomes from Mg and Zn, one or more sorts chosen from the group which M17 becomes from Si and germanium, $0 \leq j \leq 0.5$, $0 \leq k \leq 0.5$, and $0 < j+k$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices. The fluorescent substance which has the same crystal structure as a DIOPU side and a merwinite also in a fluorescent substance with the same crystal structure as the above-mentioned DIOPU side, akermanite, and a merwinite is desirable, and a fluorescent substance with the same crystal structure as a DIOPU side is still more desirable.

[0012] Next, the manufacture approach of the fluorescent substance of this invention is explained. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of calcium used as the raw material for manufacturing the fluorescent substance of this invention, the source of strontium, and a source of barium, the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material used as the source of magnesium, and the source of zinc, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material which becomes when it comes to the source of silicon, and the source of germanium, the oxide of a high grade (99% or more) can be used.

[0013] Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the europium used as an activator, and a raw material containing manganese, the oxide of a high grade (99% or more) can be used.

[0014] Especially the manufacture approach of the fluorescent substance of this invention is not limited, and can be manufactured by mixing the raw material of each above, for example, calcinating. general formula (M41-aEua) (M51-bMnb) M62O6 (M4 in a formula — calcium —) which is one of the desirable presentations one or more sorts

chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, and $0 < a + b$. The fluorescent substance which has the presentation expressed can be manufactured by carrying out weighing capacity, blending, mixing and calcinating the above-mentioned raw material so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing of these raw materials.

[0015] After mixing, the fluorescent substance of this invention is obtained by calcinating in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When what decomposes into a raw material at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can become an oxide uses it, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement. Especially as a firing environments, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1–10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air ambient atmosphere and a reducing atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0016] Furthermore, the fluorescent substance obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the fluorescent substance obtained.

[0017] High brightness is obtained by vacuum-ultraviolet-radiation excitation, and the fluorescent substance of this invention obtained as mentioned above has little brightness lowering by plasma exposure. Furthermore, in manufacture of PDP and a rare-gas lamp, although the process which installs a fluorescent substance by adding a binder to a fluorescent substance, distributing a solvent, applying to a light-emitting part, heat-treating at about 500 degrees C, and removing a binder is common, the fluorescent substance of this invention also has little brightness lowering in this heat treatment process. Therefore, since long PDP and the long rare-gas lamp of a life can be realized by high brightness when the fluorescent substance of this invention is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, it is suitable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0018] The fluorescent substance of this invention can be excited with ultraviolet rays, X-rays, electron rays, etc. other than a vacuum ultraviolet area, and can be used also for the component which made the ultraviolet rays, X-rays, and electron rays other than a vacuum ultraviolet area the source of excitation.

[0019]

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples.

[0020] Example 1 calcium carbonate CaCO_3 , a strontium carbonate (product made from Wako Pure Chem Industry) SrCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , basic-magnesium-carbonate (product made from Wako Pure Chem Industry) $(\text{MgCO}_3)4\text{Mg}(\text{OH})2.5\text{H}_2\text{O}$, (Product made from Wako Pure Chem Industry) After blending and mixing oxidation silicon (product made from Wako Pure Chem Industry) SiO_2 each raw material so that the mole ratio of $\text{CaCO}_3:\text{SrCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)4\text{Mg}(\text{OH})2.5\text{H}_2\text{O}:\text{SiO}_2$ may be set to 0.9215:0.0485:0.015:0.2:2, It calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere, and calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere again after 2-hour baking and a crack for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with $\text{Ca}0.9215\text{Sr}0.0485\text{Eu}0.03\text{MgSi}_2\text{O}_6$. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5x10⁻²Torr), blue luminescence was shown and brightness showed 24 cd/m² to this fluorescent substance.

[0021] Heat treatment was performed for the obtained fluorescent substance for 500 degrees C and 30 minutes in air. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment before, brightness did not fall at all.

[0022] The pressure installed the fluorescent substance before obtained heat treatment into the ambient atmosphere of a presentation of 5 volume %Xe–95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it expose to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with plasma exposure before, brightness did not fall at all.

[0023] Heat treatment was performed for the fluorescent substance before obtained heat treatment and plasma exposure for 500 degrees C and 30 minutes in air. Subsequently, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe–95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it exposed to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment and plasma exposure before, lowering of brightness was 4%.

[0024] Example 2 strontium carbonate SrCO_3 , a barium carbonate (product made from Wako Pure Chem Industry) BaCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , basic-magnesium-carbonate (product made from Wako Pure Chem Industry) $(\text{MgCO}_3)4\text{Mg}(\text{OH})2.5\text{H}_2\text{O}$, (Product made from Wako Pure Chem Industry) After blending and mixing oxidation silicon (product made from Wako Pure Chem Industry) SiO_2 each raw material so that the mole ratio of $\text{SrCO}_3:\text{BaCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)4\text{Mg}(\text{OH})2.5\text{H}_2\text{O}:\text{SiO}_2$ may be set to 2.28:0.57:0.075:0.2:2, It calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with $\text{Sr}2.28\text{Ba}0.57\text{Eu}0.15\text{MgSi}_2\text{O}_8$. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5x10⁻²Torr), blue luminescence was shown and brightness showed 30 cd/m² to this fluorescent substance.

[0025] The example 3 barium carbonate (product made from Kanto Chemistry) BaCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , a magnesium oxide MgO (product made from Kanto Chemistry), Oxidation silicon (Kojundo Chemical Laboratory Make) SiO_2 each raw material is blended so that the mole ratio of $\text{BaCO}_3:\text{Eu}_2\text{O}_3:\text{MgO}:\text{SiO}_2$ may be set to 1.98:0.01:1:2. Moreover, 0.1 mols added by making B–2 O₃ into flux to one mol of products, and among the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5 volume % H_2 –95 volume %Ar ambient atmosphere for 3 hours. Thus, the empirical formula obtained the fluorescent substance expressed with $\text{Ba}1.98\text{Eu}0.02\text{MgSi}_2\text{O}_7$. When

the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5x10⁻²Torr), green luminescence was shown and brightness showed 95 cd/m² to this fluorescent substance.

[0026] In manufacturing example 4(Sr_{0.99}Eu_{0.01})₂MgSi₂O₇, a strontium carbonate (product made from Kanto Chemistry) SrCO₃, oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu₂O₃, magnesium-oxide (product made from Kanto Chemistry) MgO, and oxidation silicon (Kojundo Chemical Laboratory Make) SiO₂ were used as a start raw material. These raw materials were blended so that the mole ratio of SrCO₃:Eu₂O₃:MgO:SiO₂ might be set to 1.98:0.01:1:2, and 0.1 mols added by making B-2 O₃ into flux to 2071 mol of product (Sr_{0.99}Eu_{0.01})₂MgSi₂(s), and among the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5%H₂-95%Ar ambient atmosphere for 3 hours. When the wavelength of 254nm or 365nm ultraviolet rays was irradiated, in any case, light-blue luminescence of high brightness was shown in the sample obtained after baking. When vacuum ultraviolet radiation was irradiated using the excimer 146nm lamp (USHIO, INC. make) within the vacuum tub below 6.7Pa (5x10⁻²Torr), light-blue luminescence was shown and brightness showed 2 [25cds / /] cm.

[0027] In manufacturing example 5(Sr_{0.99}Eu_{0.01})₂ZnSi₂O₇, a strontium carbonate SrCO₃, oxidation europium Eu₂O₃, a zinc oxide ZnO, and oxidation silicon SiO₂ were used as a start raw material. These raw materials were blended so that the mole ratio of SrCO₃:Eu₂O₃:ZnO:SiO₂ might be set to 1.98:0.01:1:2, 0.1 mols of B-2s O₃ were added to 2071 mol of product (Sr_{0.99}Eu_{0.01})₂ZnSi₂(s) as flux, and in the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5%H₂-95%Ar ambient atmosphere for 3 hours. The flume gap excited in ultraviolet rays (254nm or 365nm) also showed bluish green color luminescence of high brightness about the sample obtained after baking. When the excimer 146nm lamp (USHIO, INC. make) was used for the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) and vacuum ultraviolet radiation was irradiated, luminescence of a bluish green color was shown.

[0028] The example of comparison 1 calcium carbonate (product made from Wako Pure Chem Industry) CaCO₃, oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu₂O₃, basic-magnesium-carbonate (product made from Wako Pure Chem Industry) (MgCO₃)₄Mg(OH)₂·5H₂O, Oxidation silicon (product made from Wako Pure Chem Industry) SiO₂ each raw material is blended so that the mole ratio of CaCO₃:Eu₂O₃:(MgCO₃)₄Mg(OH)₂·5H₂O:SiO₂ may be set to 0.95:0.025:0.2:2. After mixing, it calcinated at the temperature of 1200 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with calcium_{0.95}Eu_{0.05}MgSi₂O₆. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5x10⁻²Torr), blue luminescence was shown and brightness showed 12 cd/m² to this fluorescent substance.

[0029] Heat treatment was performed for blue luminescence fluorescent substance BaMgAl₁₀O₁₇:Eu of example of comparison 2 marketing for 500 degrees C and 30 minutes in air. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment before, brightness fell 1%.

[0030] The pressure installed the blue luminescence fluorescent substance of the above-mentioned marketing into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it expose to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with plasma exposure before, brightness fell 25%.

[0031] Heat treatment was performed for the blue luminescence fluorescent substance of the above-mentioned marketing for 500 degrees C and 30 minutes in air. Subsequently, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it exposed to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment and plasma exposure before, brightness fell 28%.

[0032]

[Effect of the Invention] The fluorescent substance of this invention has high brightness, and there is little brightness lowering by plasma exposure, it is especially suitable for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, and since the vacuum-ultraviolet-radiation excitation light emitting device of high brightness is realizable, it is very useful industrially.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the suitable fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display panel (henceforth "PDP"), and a rare-gas lamp.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The fluorescent substance made to excite and emit light with vacuum ultraviolet radiation etc. is already known. BaMgAl₁₀O₁₇:Eu which consists of Ba, Mg, aluminum, O, and an activator (Eu) as a blue fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices for example, for example Zn₂SiO₄:Mn which consists of Zn, Si, O, and an activator (Mn) as a green fluorescent substance for example It is put in practical use as a BO₃:Eu red fluorescent substance which consists of Y, Gd, B, O, and an activator (Eu) (Y, Gd), and is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp.

[0003] However, the fluorescent substance for these vacuum-ultraviolet-radiation excitation light emitting devices was expected improvement in the further brightness. Moreover, although vacuum ultraviolet radiation is generated by discharging in rare gas and making the plasma generate in vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, by being exposed to the plasma, there is a problem to which the brightness of a fluorescent substance falls, the fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices with little brightness lowering by plasma exposure is called for, and the fluorescent substance which consists of an aluminate which was described above, a silicate, and a borate is examined. As a fluorescent substance which consists of a silicate, it is Extended, for example. abstracts of the sixth international conference on the science and technology of display Brightness was not enough although CaMgSi₂O₆:Eu was indicated by phosphors and 21-24 as a fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices. In addition, although Sr_{1.995}MgSi₂O₇:Eu_{0.005}, Dy_{0.025} and Cl_{0.025} and Sr_{0.445}Ba_{1.55}MgSi₂O₇:Eu_{0.005}, and Dy_{0.025} and Cl_{0.025} were indicated by the U.S. Pat. No. 5839718 description, it is the fluorescent substance for luminous objects used for the display of a dark place, and vacuum-ultraviolet-radiation excitation was not indicated.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The fluorescent substance of this invention has high brightness, and there is little brightness lowering by plasma exposure, it is especially suitable for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, and since the vacuum-ultraviolet-radiation excitation light emitting device of high brightness is realizable, it is very useful industrially.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention has high brightness and offering few fluorescent substances for vacuum-ultraviolet-radiation excitation light emitting devices has the brightness lowering by plasma exposure.

[Translation done.]

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- MEANS

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved under this situation, this invention persons to vacuum-ultraviolet-radiation excitation light emitting devices the inside of a silicate or a germane acid chloride fluorescent substance — general formula $mM1 O-nM2O.2M3O2$ (M1 in a formula — calcium —) One or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M2 becomes from Mg and Zn, M1 is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba at the time of one or more sorts chosen from the group which M3 becomes from Si and germanium, $0.5 \leq m \leq 3.5$, $0.5 \leq n \leq 2.5$, however $m=n=1$. Brightness is high and the silicate or germane acid chloride fluorescent substance of a specific presentation which one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator come to contain came to complete a header and this invention for there being little brightness lowering by plasma exposure.

[0006] That is, this invention relates to the following (1) – (10).

- (1) general formula $mM1 O-nM2O.2M3O2$ (M1 in a formula — calcium —) One or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M2 becomes from Mg and Zn, M1 is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba at the time of one or more sorts chosen from the group which M3 becomes from Si and germanium, $0.5 \leq m \leq 3.5$, $0.5 \leq n \leq 2.5$, however $m=n=1$. The fluorescent substance for vacuum-ultraviolet-radiation excitation light emitting devices which one or more sorts chosen from the group which becomes the compound expressed from Eu and Mn as an activator contained.
- (2) The fluorescent substance of the above-mentioned (1) publication which has the same crystal structure as a DIOPU side (Diopside, diopside).
- (3) general formula $(M41-aEua) (M51-bMnb) M62O6$ (M4 in a formula — calcium —) one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, and $0 \leq a+b$. The fluorescent substance of the above-mentioned (2) publication which has the presentation expressed.
- (4) The fluorescent substance of the above-mentioned (2) publication expressed with general formula $calcium1-c-dSrcEudMgSi 2O6$ ($0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$).
- (5) The fluorescent substance which is a fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of the above-mentioned (1) publication, and has the same crystal structure as akermanite (Akermanite, OKERUMAN stone).
- (6) general formula $(M71-eEue) 2(M81-fMnf) M92O7$ (M7 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M8 becomes from Mg and Zn, one or more sorts chosen from the group which M9 becomes from Si and germanium, $0 \leq e \leq 0.5$, $0 \leq f \leq 0.5$, and $0 \leq e+f$. The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed.
- (7) The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed with general formula $(M101-gEug) 2M11Si 2O7$ (one or more sorts chosen from the group which M10 in a formula becomes from calcium, Sr, and Ba, one or more sorts chosen from the group which M11 becomes from Mg and Zn, $0.001 \leq g \leq 0.1$).
- (8) general formula $(M121-hEuh) (M131-iMni) 2M142O7$ (M12 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M13 becomes from Mg and Zn, one or more sorts chosen from the group which M14 becomes from Si and germanium, $0 \leq h \leq 0.5$, $0 \leq i \leq 0.5$, and $0 \leq h+i$. The fluorescent substance of the above-mentioned (5) publication which has the presentation expressed.
- (9) The fluorescent substance which is a fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of the above-mentioned (1) publication, and has the same crystal structure as a merwinite (Merwinite).
- (10) general formula $(M151-jEuj) 3(M161-kMnk) M172O8$ (M15 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M16 becomes from Mg and Zn, one or more sorts chosen from the group which M17 becomes from Si and germanium, $0 \leq j \leq 0.5$, $0 \leq k \leq 0.5$, and $0 \leq j+k$. The fluorescent substance of the above-mentioned (9) publication which has the presentation expressed.

[0007]

[Embodiment of the Invention] This invention is explained in detail below. The fluorescent substance for the vacuum-ultraviolet-radiation excitation light emitting devices of this invention general formula $mM1 O-nM2O.2M3O2$ (M1 in a formula is chosen from the group which consists of calcium, Sr, and Ba — one or more sorts) At the time of one or more sorts chosen from the group which M2 becomes from Mg and Zn, one or more sorts chosen from the group which M3 becomes from Si and germanium, $0.5 \leq m \leq 3.5$, $0.5 \leq n \leq 2.5$, however $m=n=1$ M1 is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or Sr or Ba. What considers as a mother crystal, is characterized by one or more sorts chosen from the group which consists of Eu and Mn as an activator coming to contain, and has the same crystal structure as a DIOPU side, akermanite, and a merwinite is desirable.

[0008] Even in the inside in the case of having the crystal structure of a DIOPU side (Diopside, diopside) and isomorphism general formula $(M41-aEua) (M51-bMnb) M62O6$ (M4 in a formula — calcium —) which is one in $m=1$ and $n=1$ in the general formula of the above (1) one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 \leq a \leq 0.5$, $0 \leq b \leq 0.5$, and $0 \leq a+b$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting

devices. Furthermore, the fluorescent substance which has the presentation expressed with general formula $\text{Ca}_{1-c}\text{Sr}_c\text{Eu}_{1-d}\text{Mg}_d\text{Si}_2\text{O}_6$ ($0 < c \leq 0.1$, $0 < d \leq 0.1$) which is one in $m = 1$ and $n = 1$ in the general formula of the above (1), and contains calcium and Sr even in the inside in the case of having the crystal structure of a DIOPU side (Diopside, diopside) and isomorphism is still more desirable.

[0009] Even in the inside in the case of having the same crystal structure as akermanite (Akermanite, OKERUMAN stone) general formula $(\text{M}71-\text{eEu})_2(\text{M}81-\text{fMn})\text{M}92\text{O}7$ (M7 in a formula — calcium —) which is one in $m = 2$ and $n = 1$ in the general formula of the above (1) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M8 becomes from Mg and Zn, one or more sorts chosen from the group which M9 becomes from Si and germanium, $0 < e \leq 0.5$, $0 < f \leq 0.5$, and $0 < e + f$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

furthermore, the fluorescent substance which has the presentation expressed with general formula $(\text{M}101-\text{gEu})_2\text{M}11\text{Si}_2\text{O}7$ (one or more sorts chosen from the group which M10 in a formula becomes from calcium, Sr, and Ba, one or more sorts chosen from the group which M11 becomes from Mg and Zn, $0.001 \leq g \leq 0.1$) in case M9 are Si in $f = 0$ in said general formula is still more desirable.

[0010] general formula general formula $(\text{M}121-\text{hEu})_2(\text{M}131-\text{iMn})_2\text{M}142\text{O}7$ [moreover,] (M12 in a formula — calcium —) which is one in $m = 1$ and $n = 2$ in the general formula of the above (1) also in the inside in the case of having the same crystal structure as akermanite one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M13 becomes from Mg and Zn, one or more sorts chosen from the group which M14 becomes from Si and germanium, $0 < h \leq 0.5$, $0 < i \leq 0.5$, and $0 < h + i$. The fluorescent substance which has the presentation expressed is also desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0011] Even in the inside in the case of having the crystal structure of a merwinite (Merwinite) and isomorphism In the general formula of the above (1), it is one in $m = 3$ and $n = 1$. general formula $(\text{M}151-\text{jEu})_3(\text{M}161-\text{kMn})\text{M}172\text{O}8$ (M15 in a formula — calcium —) one or more sorts chosen from the group which consists of Sr and Ba, one or more sorts chosen from the group which M16 becomes from Mg and Zn, one or more sorts chosen from the group which M17 becomes from Si and germanium, $0 < j \leq 0.5$, $0 < k \leq 0.5$, and $0 < j + k$. The fluorescent substance which has the presentation expressed is desirable as an object for vacuum-ultraviolet-radiation excitation light emitting devices. The fluorescent substance which has the same crystal structure as a DIOPU side and a merwinite also in a fluorescent substance with the same crystal structure as the above-mentioned DIOPU side, akermanite, and a merwinite is desirable, and a fluorescent substance with the same crystal structure as a DIOPU side is still more desirable.

[0012] Next, the manufacture approach of the fluorescent substance of this invention is explained. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of calcium used as the raw material for manufacturing the fluorescent substance of this invention, the source of strontium, and a source of barium, the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material used as the source of magnesium, and the source of zinc, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material which becomes when it comes to the source of silicon, and the source of germanium, the oxide of a high grade (99% or more) can be used.

[0013] Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the europium used as an activator, and a raw material containing manganese, the oxide of a high grade (99% or more) can be used.

[0014] Especially the manufacture approach of the fluorescent substance of this invention is not limited, and can be manufactured by mixing the raw material of each above, for example, calcinating. general formula $(\text{M}41-\text{aEu})_2(\text{M}51-\text{bMn})\text{M}62\text{O}6$ (M4 in a formula — calcium —) which is one of the desirable presentations one or more sorts chosen from the group which two or more sorts chosen from the group which consists of Sr and Ba, Sr, or Ba and M5 become from Mg and Zn, one or more sorts chosen from the group which M6 becomes from Si and germanium, $0 < a \leq 0.5$, $0 < b \leq 0.5$, and $0 < a + b$. The fluorescent substance which has the presentation expressed can be manufactured by carrying out weighing capacity, blending, mixing and calcinating the above-mentioned raw material so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing of these raw materials.

[0015] After mixing, the fluorescent substance of this invention is obtained by calcinating in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When what decomposes into a raw material at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can become an oxide uses it, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement. Especially as a firing environments, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1-10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air ambient atmosphere and a reducing atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0016] Furthermore, the fluorescent substance obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the fluorescent substance obtained.

[0017] High brightness is obtained by vacuum-ultraviolet-radiation excitation, and the fluorescent substance of this invention obtained as mentioned above has little brightness lowering by plasma exposure. Furthermore, in manufacture of PDP and a rare-gas lamp, although the process which installs a fluorescent substance by adding a binder to a fluorescent substance, distributing a solvent, applying to a light-emitting part, heat-treating at about 500 degrees C, and removing a binder is common, the fluorescent substance of this invention also has little brightness lowering in this heat treatment process. Therefore, since long PDP and the long rare-gas lamp of a life can be realized by high brightness when the fluorescent substance of this invention is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, it is suitable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0018] The fluorescent substance of this invention can be excited with ultraviolet rays, X-rays, electron rays, etc. other than a vacuum ultraviolet area, and can be used also for the component which made the ultraviolet rays, X-rays, and electron rays other than a vacuum ultraviolet area the source of excitation.

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- EXAMPLE

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples.

[0020] Example 1 calcium carbonate CaCO_3 , a strontium carbonate (product made from Wako Pure Chem Industry) SrCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , basic-magnesium-carbonate (product made from Wako Pure Chem Industry) $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, (Product made from Wako Pure Chem Industry) After blending and mixing oxidation silicon (product made from Wako Pure Chem Industry) SiO_2 each raw material so that the mole ratio of $\text{CaCO}_3:\text{SrCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}:\text{SiO}_2$ may be set to 0.9215:0.0485:0.015:0.2:2. It calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere, and calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere again after 2-hour baking and a crack for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with calcium $0.9215\text{Sr}0.0485\text{Eu}0.03\text{MgSi}_2\text{O}_6$. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5×10^{-2} Torr), blue luminescence was shown and brightness showed 24 cd/m² to this fluorescent substance.

[0021] Heat treatment was performed for the obtained fluorescent substance for 500 degrees C and 30 minutes in air. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment before, brightness did not fall at all.

[0022] The pressure installed the fluorescent substance before obtained heat treatment into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it expose to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with plasma exposure before, brightness did not fall at all.

[0023] Heat treatment was performed for the fluorescent substance before obtained heat treatment and plasma exposure for 500 degrees C and 30 minutes in air. Subsequently, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it exposed to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment and plasma exposure before, lowering of brightness was 4%.

[0024] Example 2 strontium carbonate SrCO_3 , a barium carbonate (product made from Wako Pure Chem Industry) BaCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , basic-magnesium-carbonate (product made from Wako Pure Chem Industry) $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, (Product made from Wako Pure Chem Industry) After blending and mixing oxidation silicon (product made from Wako Pure Chem Industry) SiO_2 each raw material so that the mole ratio of $\text{SrCO}_3:\text{BaCO}_3:\text{Eu}_2\text{O}_3:(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}:\text{SiO}_2$ may be set to 2.28:0.57:0.075:0.2:2. It calcinated at the temperature of 1200 degrees C in the 2 volume % H_2 content Ar ambient atmosphere for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with $\text{Sr}_2.28\text{Ba}0.57\text{Eu}0.15\text{MgSi}_2\text{O}_8$. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5×10^{-2} Torr), blue luminescence was shown and brightness showed 30 cd/m² to this fluorescent substance.

[0025] The example 3 barium carbonate (product made from Kanto Chemistry) BaCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , a magnesium oxide MgO (product made from Kanto Chemistry), Oxidation silicon (Kojundo Chemical Laboratory Make) SiO_2 each raw material is blended so that the mole ratio of $\text{BaCO}_3:\text{Eu}_2\text{O}_3:\text{MgO}:\text{SiO}_2$ may be set to 1.98:0.01:1:2. Moreover, 0.1 mols added by making B-2 O_3 into flux to one mol of products, and among the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5 volume % H_2 -95 volume %Ar ambient atmosphere for 3 hours. Thus, the empirical formula obtained the fluorescent substance expressed with $\text{Ba}_1.98\text{Eu}0.02\text{MgSi}_2\text{O}_7$. When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5×10^{-2} Torr), green luminescence was shown and brightness showed 95 cd/m² to this fluorescent substance.

[0026] In manufacturing example 4($\text{Sr}0.99\text{Eu}0.01$) $2\text{MgSi}_2\text{O}_7$, a strontium carbonate (product made from Kanto Chemistry) SrCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , magnesium-oxide (product made from Kanto Chemistry) MgO , and oxidation silicon (Kojundo Chemical Laboratory Make) SiO_2 were used as a start raw material. These raw materials were blended so that the mole ratio of $\text{SrCO}_3:\text{Eu}_2\text{O}_3:\text{MgO}:\text{SiO}_2$ might be set to 1.98:0.01:1:2, and 0.1 mols added by making B-2 O_3 into flux to 2071 mol of product ($\text{Sr}0.99\text{Eu}0.01$) $2\text{MgSi}_2\text{O}_7$ (s), and among the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5% H_2 -95%Ar ambient atmosphere for 3 hours. When the wavelength of 254nm or 365nm ultraviolet rays was irradiated, in any case, light-blue luminescence of high brightness was shown in the sample obtained after baking. When vacuum ultraviolet radiation was irradiated using the excimer 146nm lamp (USHIO, INC. make) within the vacuum tub below 6.7Pa (5×10^{-2} Torr), light-blue luminescence was shown and brightness showed 2 [25cds / /] cm.

[0027] In manufacturing example 5($\text{Sr}0.99\text{Eu}0.01$) $2\text{ZnSi}_2\text{O}_7$, a strontium carbonate SrCO_3 , oxidation europium Eu_2O_3 , a zinc oxide ZnO , and oxidation silicon SiO_2 were used as a start raw material. These raw materials were blended so

that the mole ratio of $\text{SrCO}_3\text{:Eu}_2\text{O}_3\text{:ZnO:SiO}_2$ might be set to 1.98:0.01:1:2, 0.1 mols of B-2s O3 were added to 2071 mol of product ($\text{Sr}_{0.99}\text{Eu}_{0.01}$) 2ZnSi(s) as flux, and in the acetone, with the mortar, wet blending was carried out enough and it dried. The obtained mixed raw material was paid to the metal mold made from stainless steel, and it pressurized by the pressure of 40MPa, and fabricated on the circular pellet with a diameter [of 15mm] x thickness of 3mm. The obtained pellet was put into alumina crucible and it calcinated at 1200 degrees C in the 5%H₂-95%Ar ambient atmosphere for 3 hours. The flume gap excited in ultraviolet rays (254nm or 365nm) also showed bluish green color luminescence of high brightness about the sample obtained after baking. When the excimer 146nm lamp (USHIO, INC. make) was used for the fluorescent substance obtained within the vacuum tub below 6.7Pa (5x10⁻²Torr) and vacuum ultraviolet radiation was irradiated, luminescence of a bluish green color was shown.

[0028] The example of comparison 1 calcium carbonate (product made from Wako Pure Chem Industry) CaCO_3 , oxidation europium (Shin-Etsu Chemical Co., Ltd. make) Eu_2O_3 , basic-magnesium-carbonate (product made from Wako Pure Chem Industry) MgCO_3 $4\text{Mg(OH)2.5H}_2\text{O}$, Oxidation silicon (product made from Wako Pure Chem Industry) SiO_2 each raw material is blended so that the mole ratio of $\text{CaCO}_3\text{:Eu}_2\text{O}_3\text{:MgCO}_3\text{:}4\text{Mg(OH)2.5H}_2\text{O:SiO}_2$ may be set to 0.95:0.025:0.2:2. After mixing, it calcinated at the temperature of 1200 degrees C in the 2 volume %H₂ content Ar ambient atmosphere for 2 hours. Thus, the empirical formula obtained the fluorescent substance expressed with calcium_{0.95}Eu_{0.05}MgSi 2O_6 . When the excimer 146nm lamp (the USHIO, INC. make, H0012 mold) was used for the obtained fluorescent substance and ultraviolet rays were irradiated within the vacuum tub below 6.7Pa (5x10⁻²Torr), blue luminescence was shown and brightness showed 12 cd/m² to this fluorescent substance.

[0029] Heat treatment was performed for blue luminescence fluorescent substance $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ of example of comparison 2 marketing for 500 degrees C and 30 minutes in air. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment before, brightness fell 1%.

[0030] The pressure installed the blue luminescence fluorescent substance of the above-mentioned marketing into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it expose to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with plasma exposure before, brightness fell 25%.

[0031] Heat treatment was performed for the blue luminescence fluorescent substance of the above-mentioned marketing for 500 degrees C and 30 minutes in air. Subsequently, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and, subsequently to the plasma of 50W, made it exposed to the plasma of 10W for 15 minutes for 30 minutes. As a result of taking out a fluorescent substance and measuring brightness, as compared with heat treatment and plasma exposure before, brightness fell 28%.

[Translation done.]